Properties of Multifunctional Hybrid Carbon Nanotube/Carbon Fiber Polymer Matrix Composites

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ABSTRACT

For aircraft primary structures, carbon fiber reinforced polymer (CFRP) composites possess many advantages over conventional aluminum alloys due to their light weight, higher strength- and stiffness-to-weight ratios, and low life-cycle maintenance costs. However, the relatively low electrical and thermal conductivities of CFRP composites fail to provide structural safety in certain operational conditions such as lightning strikes. Carbon nanotubes (CNT) offer the potential to enhance the multi-functionality of composites with improved thermal and electrical conductivity. In this study, hybrid CNT/carbon fiber (CF) polymer composites were fabricated by interleaving layers of CNT sheets with Hexcel® IM7/8852 prepreg. Resin concentrations from 1 wt% to 50 wt% were used to infuse the CNT sheets prior to composite fabrication. The interlaminar properties of the resulting hybrid composites were characterized by mode I and II fracture toughness testing. Fractographical analysis was performed to study the effect of resin concentration. In addition, multi-directional physical properties like thermal conductivity of the orthotropic hybrid polymer composite were evaluated.

Keywords: Hybrid Composites, Carbon Nanotubes, Carbon Fiber, Composites

1 INTRODUCTION

The Boeing 787 dreamliner and the Airbus A350 XWB feature approximately 50% CFRP by structural weight [1-2]. However, CFRP airframes suffer from several problems in connection with lightning strike damage. Commercial airplanes experience one lightning strike for every 1,000 to 10,000 hours of flight or one or two strikes a year [2-3]. Compared to traditional aluminum structures, CFRPs possess lower electrical and thermal conductivities and are unable to dissipate the electrical current and thermal energy effectively [2]. For lightning strike protection (LSP), major aerospace companies utilize metallic woven mesh embedded beneath the paint scheme as a sacrificial layer which can dissipate the electrical and thermal energy by ablation during a lighting strike [3,4].

An alternative method of LSP for CFRP is to improve the electrical and thermal conductivity of the composite without degrading the mechanical strength by incorporating carbon nanotubes (CNTs) [1,3-7]. However, there are still interfacial problems that exist between CNTs [or carbon fiber (CF)] and the resin due to the manufacturing process not being fully optimized. In addition, it is important to understand the orthotropic properties along the three orthogonal directions (axial, perpendicular to axial/in-plane, and perpendicular to axial/out-of-plane) of unidirectional hybrid CNT/CF composite. In this paper, the effect of CNT and resin concentration on the interfacial strength of hybrid CNT/CF polymer composites was investigated by evaluating mode I and II fracture toughness. In addition, the directional physical properties of thermal conductivity were evaluated.

2 EXPERIMENTAL

2.1 Materials Hexcel IM7/8552 prepreg (12k, 145 g/m^2, 35% resin content) was used for preparing hybrid CNT/CF polymer composites. The cured ply thickness is reported to be 0.131 mm [1,8]. CNT sheet [Lot# 71019, single walled- (SW-) and few walled-CNT (FWCNT), acetone condensed] was purchased from Nanocomp Technologies, Inc., Merrimack, NH. Average areal density of the CNT sheet was 9.8 g/m^2. The CNT sheets possess an inherent directionality due to the drawing process, and this processing direction (MD) was termed the 0° direction [1]. A commercial toughened epoxy resin (API-60, Applied Poleramic, Inc., Benicia, CA), which has similar properties to Hexcel 8552, was used to pre-impregnate the CNT sheets. Methyl ethyl ketone (MEK, Sigma-Aldrich, St. Louis, MO) and cyclohexanone (Sigma-Aldrich, St. Louis, MO) were used as received to make dilute API-60 resin solutions.

2.2 Hybrid CNT/CF Composite Fabrication Hybrid CNT/CF polymer composites were fabricated following the Langley Research Center (LaRC) developed procedure [1,9]. Various concentrations of toughened epoxy resin solution were prepared by dissolving API-60 epoxy resin in either MEK to make up a 50wt% solution or in a mixture of MEK and cyclohexanone (1:3 ratio) for 1 and 5wt% solutions. The predetermined amount of API-60 solution was painted on the CNT sheets resulting in "pre-infused" CNT/epoxy prepreg sheet with desirable weight fractions of CNT (60, 75 and 95wt%) after vacuum drying at room temperature overnight. To prepare stretched CNT sheets, the CNT sheet was stretched to 121% of its original length using a mechanical extension apparatus [9]. The pre-infused CNT/epoxy prepreg sheets were used for further fabrication of hybrid CNT/CF composites. For double cantilever beam (DCB) and end notch flexure (ENF) coupons, panels (30.5 × 30.5cm) with 32 plies of IM7/8552 prepreg were fabricated by interleaving aligned, pre-infused CNT/epoxy prepreg sheets (7.6 × 7.6cm) adjacent to the 12.5μm thick Teflon® film as a crack-starter between the 16th and 17th plies of IM7/8552 prepreg. Sample nomenclature used was TEST-CNT%-Resin Solution%-Stretch/No Stretch. For thermal conductivity test coupons, 80 plies of IM7/8552 prepreg were aligned with the 0° direction of the carbon fibers to get a panel (7.6 × 7.6cm) by interleaving 80 plies of pre-infused CNT prepreg sheet between IM7/8552 prepreg sheets. The stack of hybrid prepreg plies was placed in a stainless steel mold with the 0° direction of the CNT sheets aligned with the 0° direction of the carbon fibers, and cured in a vacuum hot press according to a recommended Hexcel cure process. After cure, the panels were cut along the three orthogonal directions by a wet-saw and polished for each orthotropic property test.

2.3 Fracture Toughness Characterization

2.3.1 Mode I Interlaminar Fracture Toughness Mode I double cantilever beam (DCB) test coupons were fabricated and tested according to ASTM D5528 [1,10]. A MTS-858 table-top servo-hydraulic test frame with a 2250 N load cell was used. Displacement was controlled at a rate of 1.27 mm/min until the crack propagated 40 mm. Mode I fracture toughness (G_{IC}) was calculated using the Modified Beam Theory (MBT) since it yields more conservative values compared to the other methods such as compliance methods or a modified compliance calibration method [1,10-11].

2.3.2 Mode II Interlaminar Shear Fracture Toughness Mode II interlaminar shear fracture toughness (G_{IIC}) of the composites was characterized using the end notch flexure (ENF) test method described in References 1 and 12.

2.4 Directional Physical Property Characterization

2.4.1 Sample Preparation Hybrid CNT/unidirectional CF epoxy polymer composites have orthotropic thermal conductivity properties. The axial (1-), perpendicular/in-plane direction (2-), and perpendicular/out-of-plane (3-) direction to the CF alignment formed the orthogonal principal directions for unidirectional hybrid composites as shown in Figure 1. Thick (approximately 13 ~ 16 mm) composite panels of 80 plies of control CF composite ($[0]_{80}$) and 160 plies of hybrid CNT/CF polymer composite ($[0/CNT]_{80}$) were cut along the three orthogonal directions as shown in Figure 1.

2.4.2 Thermal Conductivity Characterization Thermal conductivity was calculated by measuring thermal diffusivity according to ASTM E1461-13 [13]. The thermal diffusivity (λ) was measured by laser flash method using a Netzsch LFA-457 MicroFlash® with the correction factor suggested by Cowan (K_c) for the heat loss and non-uniform heating effect correction [11].

The specific heat (C_p) was measured by modulated differential scanning calorimetry using a Netzsch DSC 204 F1 Phoenix®. Pyroceram 9606 with Inconel was used as a reference material for the thermal diffusivity and specific heat measurements.

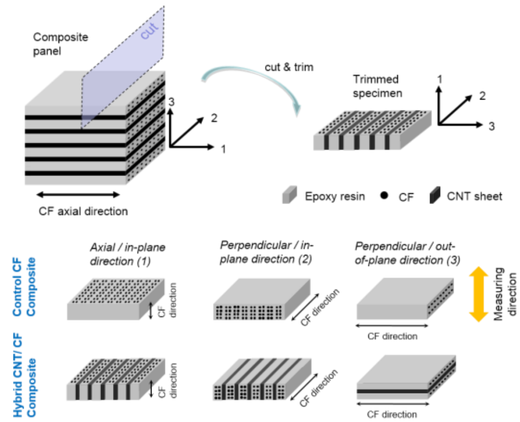


Figure 1. Preparation of orthotropic thermal conductivity test specimens.

2.5 Fractographical Analysis The morphology of the failed specimens was studied using a Hitachi S-5200 field-emission scanning electron microscope (FE-SEM). The accelerating voltage and beam current were 25-30 KeV and 17-20 μA, respectively. The specimens were polished as needed.

3 RESULTS AND DISCUSSION

3.1 CNT Sheets Figure 2 shows a scanning electron microscope (SEM) image of an as-received CNT sheet. Tensile strength and strain were reported as 430.2 ± 18.4 MPa and 45.8 ± 3.5 %, respectively, by the manufacturer. Figure 3 shows the cross-sectional image of a CNT sheet interleaved between CF/epoxy plies within the hybrid CNT/CF polymer composite.

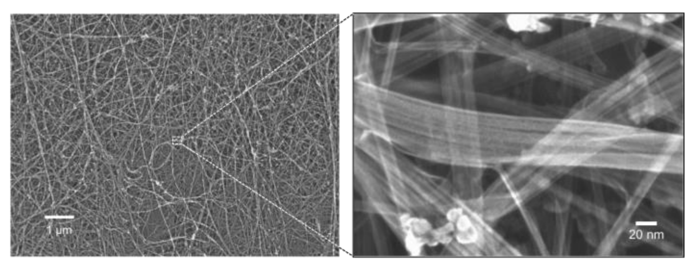


Figure 2. SEM images of as-received CNT sheet.

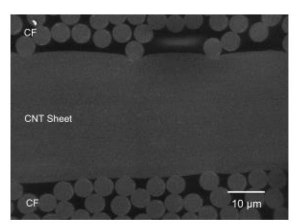


Figure 3. Cross-sectional SEM image of interleaved CNT sheet between CF/epoxy plies.

3.2 Mode I and Mode II Fracture Toughness Characterization Mode I interlaminar fracture toughness (G_{IC}) of control CF composites and hybrid CNT/CF polymer composites are shown in Figure 4. All of the hybrid CNT/CF polymer composites showed lower G_{IC} values than the control CF composite. In this study, investigation of the effect of resin concentration was intended to determine the processing conditions which will be used as the baseline for future interfacial enhancement studies. The resin concentration of the pre-infusion process and the CNT concentration in the pre-infused CNT/epoxy prepreg sheets did not have a significant effect on mode I fracture toughness. The interleaved stretched CNT sheet hybrid polymer composite (DCB-60-5-S) did not show any noticeable difference as well.

In comparison with the mode I interlaminar fracture toughness, the interleaved CNT sheets yielded promising results in the mode II interlaminar shear fracture toughness (G_{IIC}) evaluated by an ENF test as shown in Figure 5. While the G_{IIC} of the control CF composite was 677.68 ± 71.8 J/m^2, the G_{IIC} of the hybrid CNT/CF polymer composites were between 756.27 and 1101.60 J/m^2, showing an increase of approximately 12% to 63%. In addition, the stretched CNT sheet showed a higher enhancement compared to the non-stretched CNT sheet. The stretched CNT seemed to absorb more energy during shear fracture as shown in the SEM image of fracture surfaces [Figure 6 (a-b) for the non-stretched CNT composite, Figure 6 (c-d) for the stretched CNT composite]. This result was consistent with the previous work which showed a positive effect of CNT sheet on mode II fracture toughness [1,6-7]. However, the resin concentration for pre-infusion did not show any significant influence. In addition, the effect of CNT concentration in the pre-infused CNT/epoxy prepreg sheets on the mode II interlaminar shear fracture toughness was not significant. The 95wt% CNT concentration does not result in uniform infusion of the sheet using the current method. The fracture surface of the ENF-95-1-NS revealed dry CNT fibrils compared to the other sample surfaces [Figure 6 (e-f)].

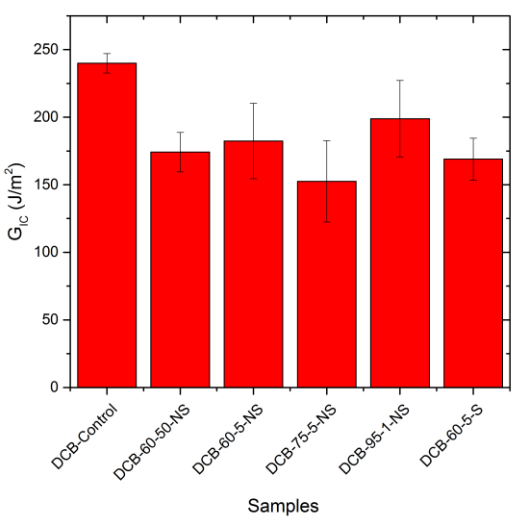


Figure 4. Mode I interlaminar fracture toughness (G_{IC}) of control CF and CNT/CF hybrid composites.

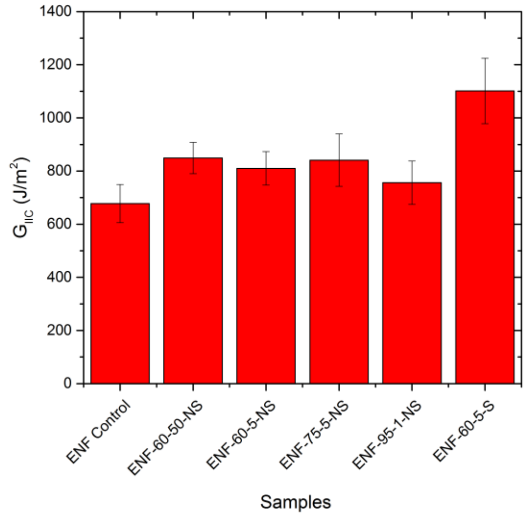


Figure 5. Mode II interlaminar shear fracture toughness (G_{IIC}) of control CF and hybrid CNT/CF composites.

3.3 Orthotropic Thermal Conductivities Test specimens were prepared to evaluate the directional properties as shown in Figure 1. Volume fraction of the interleaved CNT sheets was 22.5% v/v.

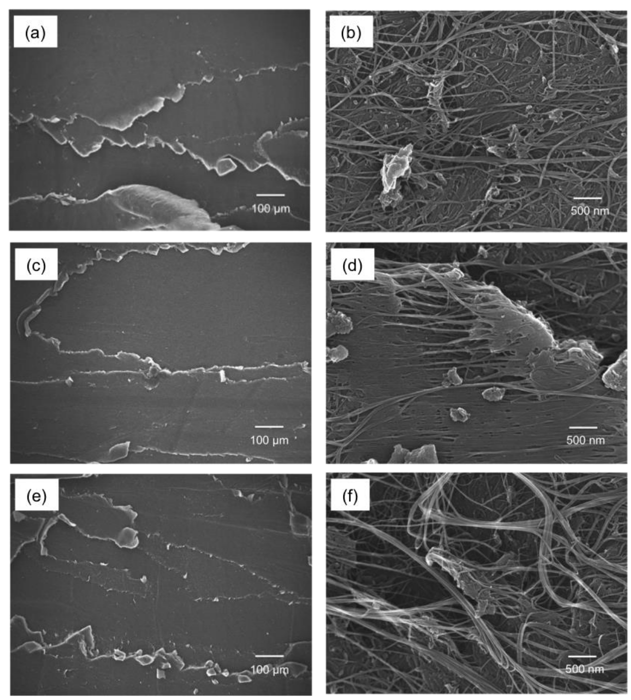
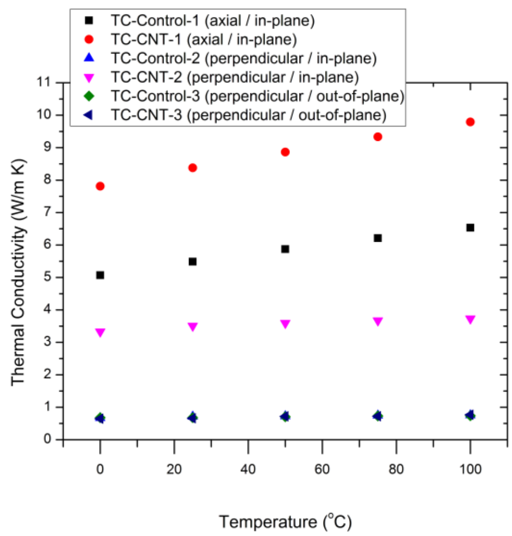


Figure 6. SEM images of fracture surfaces of (a-b) ENF-60-50-NS, (c-d) ENF-60-5-S, and (e-f) ENF-95-1-NS.

Multi-directional thermal conductivities of the control CF and the hybrid CNT/CF composites are shown in Figure 7. The thermal conductivity in the axial direction of the control CF composite (λ_1) was as high as 5.49 W/m·K at 25°C, similar to other literature values, due to direct thermal conduction through the axial CF [1,2]. However, the transverse thermal conductivities in-plane and out-of-plane (λ_2 and λ_3) were as low as approximately 0.7 W/m·K at 25°C due to the high thermal resistance of the resin and the high phonon scattering between the CF and epoxy resin. All the directional thermal conductivities of the control CF composites increased linearly with increasing temperature between 0°C to 100°C. When CNT sheets were interleaved between the CF plies, the in-plane thermal conductivities of the hybrid CNT/CF polymer composites significantly increased to as high as 8.38 W/m·K for λ_1 and 3.51 W/m·K for λ_2, resulting in approximately a 50 to 400% increase, respectively. This enhancement in thermal conductivity likely originated from the inherent high thermal conductivity of CNTs. However, the out-of-plane thermal conductivity (λ_3) did not exhibit any noticeable increase with the interleaved CNT sheets because of the high thermal resistance and phonon scattering between interfaces of the CNT, CF and resin.



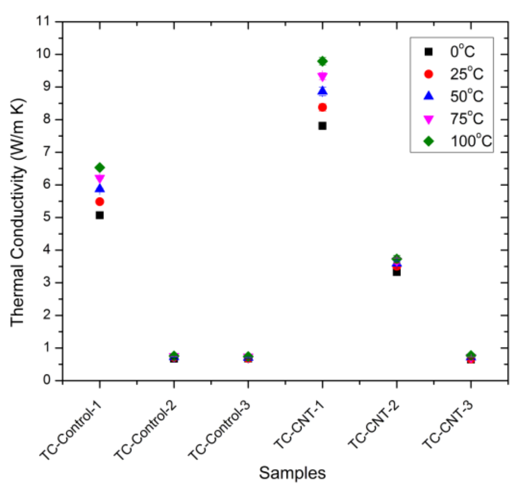


Figure 7. Orthotropic thermal conductivities (λ_1, λ_2 and λ_3) of control CF composites and hybrid CNT/CF composites.

4 CONCLUSIONS

Hybrid CNT/CF polymer composites were fabricated by interleaving layers of CNT sheets between Hexcel® IM7/8852 prepreg plies. The effects of CNT sheet and resin concentration for pre-infusion of CNT sheet on the interlaminar fracture toughness were investigated by evaluating the mode I and mode II fracture toughness using DCB and ENF tests. While the infused CNT sheet degraded mode I fracture toughness (G_{IC}), the infused CNT sheet enhanced interlaminar shear fracture toughness (G_{IIC}) by about 12 ~ 63% compared to the control CF composite. A greater enhancement was observed when the CNT sheet was stretched. Resin concentration for pre-infusion did not have significant influence on mode I or II fracture toughness. Poor interfacial interaction between the CNT and resin was confirmed by fractographical analysis. These results will be utilized as a baseline for further interfacial enhancement studies.

Orthotropic thermal conductivities of the control CF composite and the hybrid CNT/CF polymer composite were characterized with multi-directional test specimens. Compared to the control CF composite, hybrid CNT/CF polymer composites exhibited approximately 50 to 400% increase in in-plane thermal conductivity of axial (1-direction) and perpendicular to axial (2-direction) directions. However, the out-of-plane (3-direction) thermal conductivity did not show any noticeable change with the interleaved CNT sheets presumably because of the large thermal resistance and phonon scattering at the interfaces of the CNT, CF and resin.

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